Acid-Catalyzed Oxidative Addition of Thiols to Olefins and Alkynes for a One-Pot Entry to Sulfoxides

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Supporting Information

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**Experimental details**

Unless otherwise indicated, all starting materials, reagents and solvents were purchased from commercial distributors and used as received. The acrylamide starting materials (N-methyl-N-phenylacrylamide, N-phenylacrylamide and N-phenylmethacrylamide) were synthesized according to a reported procedure.\[^1\] Solvents (hexanes, acetone) used for column chromatography were of technical grade and used after distillation in a rotary evaporator. THF was dried over sodium/benzophenone then distilled and stored under Ar gas for moisture sensitive reactions.

TLC was used to check the reactions for full conversion and was performed on Macherey-Nagel Polygram Sil G/UV\textsubscript{254} thin layer plates. TLC spots were visualized by UV-light irradiation.

Flash column chromatography was carried out using Merck Silica Gel 60 (40-63 μm). Yields refer to pure isolated compounds.

\(^1\)H and \(^{13}\)C NMR spectra were measured with Bruker AV 500 spectrometers. All chemical shifts are given in ppm downfield relative to TMS and were referenced to the solvent residual peaks.\[^2\] \(^1\)H NMR chemical shifts are designated using the following abbreviations as well as their combinations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, app. = apparent. For \(^{13}\)C NMR data the following abbreviations are used: p = primary (\(CH_3\)), s = secondary (\(CH_2\)), t = tertiary (\(CH\)), q = quaternary (C).

High resolution mass spectra were recorded with a Bruker APEX III FTICR-MS or a Finnigan SSQ 7000 quadrupole MS or a Finnigan MAT 95 double focusing sector field MS instrument.

**Abbreviations:** MsOH: methanesulfonic acid; TfOH: trifluormethanesulfonic acid; TsOH: p-Toluenesulfonic acid; TFA: Trifluoromethanesulfonate; Me: methyl; Ph: phenyl; DCM: dichloromethane; EtOAc: ethyl acetate; THF: tetrahydrofurane; MeCN: acetonitrile; EtOH: ethanol

**Warning:**
Although we never experienced any problems in working with or handling tert-butyl hydroperoxide (commercial solution in decane) as described in this work, precautions should be taken when working with peroxides. In particular, it should be avoided as much as possible to expose neat peroxides or even the commercial solution to heat or to mix them undiluted with metals or metal salts. Performing such reactions behind a blast shield is recommended. In this report, the peroxide solution was generally added to the reagents in solvent and the catalyst was added last; we did not encounter any problems using this approach.
Full details of the optimisation of reaction conditions

For the optimization of reaction conditions, the reactions were performed as follows:

To a 1 mL screw cap vial charged with a magnetic stirring bar, dry acetonitrile (0.5 ml), styrene (0.5 mmol, 1 equivalent), thiophenol (1.0 mmol, 2 equiv.) and oxidant (generally tBuOOH as a 5.5M solution in decane, 1.5 mmol, 3 equiv.) were added in that order. To the solution, the catalyst (10 mol%) was added and the reaction mixture was heated at 40°C (in an aluminum heating block) and stirred at 300 rpm. The vials were closed and only contained a small headspace of air, no special treatment was used to exclude air or moisture. After the time indicated in Table S1, a defined amount of 1,3,5-trimethylbenzene was added as internal standard. After that, an aliquot of the reaction mixture was taken and the solvent was removed under vacuum. The resulting residue was taken up in deuterated DMSO and analyzed by 1H-NMR, calculating the yields of the products relative to the internal standard.

The full results are shown in Table S1.

Using 0.5 equivalents of tBuOOH, the sulfoxide product 1a was generated in 48% yield (Table S1, entry 1). Increasing the amount of oxidant could improve the yield and the reaction rate (entries 2-3). Subsequently, the catalytic activity of other catalysts was investigated in MeCN. Besides MsOH, p-Toluenesulfonic acid (TsOH), HClO4, H2SO4, trifluoroacetic acid (TFA), and HNO3 could also efficiently catalyze this oxidative addition reaction (entries 4-8). The weak Brønsted acid AcOH and the redox-active metal salts CuCl2, CuBr, and FeCl2 did give very poor selectivities and conversions, respectively (entries 8-12). AgOTf and CoCl2 were found to be more suitable metal salt catalysts, but were less successful than MsOH (entries 13-14). The best yield (95%) was obtained by employing 10 mol% MsOH and 3.0 equivalents tBuOOH (entry 15). Reducing the thiophenol loading from 2 to 1.2 equivalents, or decreasing acid loading from 10 to 2.5 mol% gave slightly inferior results (entries 16-18). By using aqueous H2O2 (35%) instead of tBuOOH, only traces of the thiol-ene product were formed (entry 19). Low yield (34%) of sulfoxide 1a was generated in the absence of acid, and only the sulfide 2a was observed in the absence of oxidant (entries 20-22).

A slight accelerating effect of tBuOOH on the addition reaction can be observed from the effect of varying its concentration. For example, nearly full conversion of styrene is achieved after 8 hours in the presence of 3 equiv. of tBuOOH (entry 15), but only after 14-20 hours in the presence of 2 equiv. (entries 3, 4). In the presence of 0.5 equivalents or without, 20 hours are necessary to achieve high conversions (entries 1, 21, 22).
Table S1. Optimization of the reaction conditions\textsuperscript{a})

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol %)</th>
<th>Oxidant (equiv)</th>
<th>Yield of 1a (%)\textsuperscript{b)}</th>
<th>Yield of 2a (%)\textsuperscript{b)}</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MsOH (10)</td>
<td>TBHP (0.5)</td>
<td>48</td>
<td>21</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>MsOH (10)</td>
<td>TBHP (1)</td>
<td>79</td>
<td>14</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>MsOH (10)</td>
<td>TBHP (2)</td>
<td>92</td>
<td>trace</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>TsOH (10)</td>
<td>TBHP (2)</td>
<td>91</td>
<td>trace</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>HClO\textsubscript{4} (10)</td>
<td>TBHP (2)</td>
<td>84</td>
<td>trace</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>H\textsubscript{2}SO\textsubscript{4} (10)</td>
<td>TBHP (2)</td>
<td>77</td>
<td>trace</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>HNO\textsubscript{3} (10)</td>
<td>TBHP (2)</td>
<td>79</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>8</td>
<td>CF\textsubscript{3}CO\textsubscript{2}H</td>
<td>TBHP (2)</td>
<td>76</td>
<td>17</td>
<td>14</td>
</tr>
<tr>
<td>9</td>
<td>AcOH (10)</td>
<td>TBHP (2)</td>
<td>55</td>
<td>34</td>
<td>14</td>
</tr>
<tr>
<td>10</td>
<td>CuCl\textsubscript{2} (10)</td>
<td>TBHP (3)</td>
<td>11</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>11</td>
<td>CuBr (10)</td>
<td>TBHP (3)</td>
<td>13</td>
<td>29</td>
<td>8</td>
</tr>
<tr>
<td>12</td>
<td>FeCl\textsubscript{2} (10)</td>
<td>TBHP (3)</td>
<td>-</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>13</td>
<td>AgOTf (10)</td>
<td>TBHP (3)</td>
<td>65</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>14</td>
<td>CoCl\textsubscript{2} (10)</td>
<td>TBHP (3)</td>
<td>69</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>15</td>
<td>MsOH (10)</td>
<td>TBHP (3)</td>
<td>95</td>
<td>trace</td>
<td>8</td>
</tr>
<tr>
<td>16</td>
<td>MsOH (10)\textsuperscript{c)}</td>
<td>TBHP (2)</td>
<td>91</td>
<td>trace</td>
<td>18</td>
</tr>
<tr>
<td>17</td>
<td>MsOH (5)</td>
<td>TBHP (2)</td>
<td>85</td>
<td>trace</td>
<td>18</td>
</tr>
<tr>
<td>18</td>
<td>MsOH (2.5)</td>
<td>TBHP (2)</td>
<td>88</td>
<td>7</td>
<td>18</td>
</tr>
<tr>
<td>19</td>
<td>MsOH (10)</td>
<td>H\textsubscript{2}O\textsubscript{2} (3)</td>
<td>-</td>
<td>trace</td>
<td>8</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>TBHP (2)</td>
<td>34</td>
<td>30</td>
<td>18</td>
</tr>
<tr>
<td>21</td>
<td>MsOH (10)</td>
<td>-</td>
<td>-</td>
<td>98</td>
<td>20</td>
</tr>
<tr>
<td>22</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99</td>
<td>20</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} Reaction conditions: styrene (0.5 mmol), thiophenol (1 mmol), solvent (0.5 mL), 40°C, 8-24h. \textsuperscript{b)} Yields were determined by \textsuperscript{1}H NMR analysis of the crude reaction mixture using using 1,3,5-trimethylbenzene as internal standard. \textsuperscript{c)} thiophenol (0.6 mmol)

The screening of a range of solvents showed that the reaction in polar solvents such as MeCN, EtOH, AcOEt, Dioxan, THF or acetone performed significantly better than in the nonpolar solvents toluene, CH\textsubscript{2}Cl\textsubscript{2} or hexane. Acetonitrile was found to be optimal (Table S2).
Table S2. Effect of Solvents on the reaction under optimised conditions a)

![Chemical Reaction Diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>1a Yield (%)b</th>
<th>2a Yield (%)b</th>
<th>Time(h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>95</td>
<td>trace</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>DMSO</td>
<td>29</td>
<td>68</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>EtOH</td>
<td>90</td>
<td>trace</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>AcOEt</td>
<td>86</td>
<td>trace</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Hexane</td>
<td>6</td>
<td>trace</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>CH₂Cl₂</td>
<td>5</td>
<td>trace</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>CHCl₃</td>
<td>6</td>
<td>trace</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>Toluene</td>
<td>34</td>
<td>trace</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>Dioxan</td>
<td>84</td>
<td>trace</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>THF</td>
<td>83</td>
<td>trace</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>Acetone</td>
<td>73</td>
<td>trace</td>
<td>18</td>
</tr>
</tbody>
</table>

a) Reaction conditions: styrene (0.5 mmol), thiophenol (1 mmol), solvent (0.5 mL), MsOH (10 mol%), TBHP (3 equiv.), 40°C. b) Yields were determined by ^1^HNMR analysis of the crude reaction mixture using using 1,3,5-trimethylbenzene as internal standard.

Increased reaction temperatures did not lead to improved yields and at 80°C and above, increased amounts of sulfone byproduct 44a were detected (Table S3).
**Table S3. Effect of temperature on the reaction under optimised conditions**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature</th>
<th>1a Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>2a Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>44a Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>r.t.&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>88</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>r.t.&lt;sup&gt;c&lt;/sup&gt;</td>
<td>23</td>
<td>68</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>r.t.</td>
<td>83</td>
<td>8</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>r.t.</td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>92</td>
<td>-</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>70</td>
<td>-</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>61</td>
<td>-</td>
<td>28</td>
<td>8</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>51</td>
<td>-</td>
<td>31</td>
<td>8</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: styrene (0.5 mmol), thiophenol (1 mmol), MeCN (0.5 mL), MsOH (10 mol%), TBHP (3 equiv.).<br><sup>b</sup> Yields were determined by 1H NMR analysis of the crude reaction mixture using using 1,3,5-trimethylbenzene as internal standard.<br><sup>c</sup> Without MsOH.
**Substrates failing to afford desired sulfoxides**
The alkenes and thiols shown below did not give the sulfoxide products under standard conditions.

![Alkenes and Thiols](image)

**Mechanistic control experiments**
The experiments shown below were conducted to gain additional information regarding the reaction mechanism:

![Mechanistic Control Experiments](image)
Synthesis of products

General procedure:
To a 1 mL screw cap vial charged with a magnetic stirring bar, dry acetonitrile (0.5 ml), the olefin substrate (0.5 mmol, 1 equivalent), the thiol substrate (1.0 mmol, 2 equiv.) and iBuOOH (5.5M solution in decane, 1.5 mmol, 3 equiv.) were added in that order. To the solution, methanesulfonic acid (3.55 μL, 10 mol%) was added and the reaction mixture was heated at 40°C (in an aluminum heating block) and stirred at 300 rpm. The vials were closed and only contained a small headspace of air, but no special treatment was necessary to exclude air or moisture. The reaction mixtures were analyzed by thin-layer-chromatography in order to determine the time when full conversion was reached. The reaction mixture was diluted, a small amount of silica was added and the solvent was removed under vacuum. The resulting powder was purified by column chromatography on silica gel using mixtures of hexane and acetone to afford the desired product.

(Phenethylsulfinyl)benzene (1a)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 102 mg (89% yield).

\[
\begin{align*}
\text{Ph} & \quad \text{S} \\
& \quad \text{S} \\
\end{align*}
\]

\(^1\text{H NMR:}\) (CDCl\(_3\); 500 MHz): 7.64-7.62 (m, 2H); 7.54-7.48 (m, 3H); 7.29-7.26 (m, 2H); 7.22-7.16 (m, 3H); 3.12-2.99 (m, 3H); 2.91-2.86 (m, 1H)

\(^13\text{C NMR:}\) (CDCl\(_3\); 125 MHz): 143.63 (Ar q); 138.77 (Ar q); 131.05 (Ar CH); 129.30 (Ar CH); 128.76 (Ar CH); 128.57 (Ar CH); 126.72 (Ar CH); 124.02 (Ar CH); 58.33 (CH\(_2\)); 28.19 (CH\(_2\))

HRMS (ESI): Calculated for [C\(_{14}\)H\(_{14}\)OSNa\(^+\)]\(^{\text{M+Na}^+}\); 253.065756; found: 253.065900

1-Fluoro-4-(2-(phenylsulfinyl)ethyl)benzene (1b)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as clear oil, 107 mg (86% yield).

\[
\begin{align*}
\text{Ph} & \quad \text{S} \\
& \quad \text{S} \\
\end{align*}
\]

\(^1\text{H NMR:}\) (CDCl\(_3\); 500 MHz): 7.61-7.59 (m, 2H); 7.52-7.47 (m, 3H); 7.12-7.10 (m, 2H); 6.96-6.92 (m, 2H); 3.09-2.94 (m, 3H); 2.87-2.81 (m, 1H)

\(^13\text{C NMR:}\) (CDCl\(_3\); 125 MHz): 160.60 (d, J=244.8 Hz, Ar q); 142.39 (Ar q); 133.31 (d, J=3.2 Hz, Ar q); 130.02 (Ar CH); 128.97 (d, J=7.8 Hz, Ar CH); 128.25 (Ar CH); 122.90 (Ar CH); 114.49 (d, J=21.3 Hz, Ar CH); 57.23 (CH\(_2\)); 26.32 (CH\(_2\))

HRMS (ESI): Calculated for [C\(_{14}\)H\(_{13}\)OFNa\(^+\)]\(^{\text{M+Na}^+}\); 271.056335; found: 271.056430
1-Chloro-4-(2-(phenylsulfinyl)ethyl)benzene (1c)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 119 mg (90% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.62-7.60 (m, 2H); 7.52-7.49 (m, 3H); 7.24-7.23 (m, 2H); 7.10-7.09 (m, 2H); 3.09-2.95 (m, 3H); 2.87-2.83 (m, 1H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 143.42 (Ar q); 137.21 (Ar q); 132.54 (Ar q); 131.13 (Ar CH); 129.94 (Ar CH); 129.34 (Ar CH); 128.87 (Ar CH); 123.98 (Ar CH); 58.01 (CH$_2$); 27.50 (CH$_2$)

HRMS (ESI): Calculated for [C$_{14}$H$_{13}$OClSNa]$^+$ (M+Na$^+$): 287.026785; found: 287.026900

1-Bromo-4-(2-(phenylsulfinyl)ethyl)benzene (1d)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 151 mg (98% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.61-7.59 (m, 2H); 7.51-7.49 (m, 3H); 7.38-7.37 (m, 2H); 7.03-7.02 (m, 2H); 3.07-2.93 (m, 3H); 2.84-2.78 (m, 1H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 143.41 (Ar q); 137.73 (Ar q); 131.83 (Ar CH); 131.13 (Ar CH); 130.32 (Ar CH); 129.35 (Ar CH); 123.98 (Ar CH); 120.58 (Ar q); 57.93 (CH$_2$); 27.56 (CH$_2$)

HRMS (ESI): Calculated for [C$_{14}$H$_{13}$OBrSNa]$^+$ (M+Na$^+$): 330.976282; found: 330.976540

4-(2-(Phenylsulfinyl)ethyl)benzonitrile (1e)
Synthesized according to the general procedure, using a 7/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 110 mg (86% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.61-7.59 (m, 2H); 7.56-7.49 (m, 5H); 7.28-7.26 (m, 2H); 3.19-3.13 (m, 1H); 3.10-3.04 (m, 1H); 3.01-2.88 (m, 2H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 144.42 (q); 143.12 (Ar q); 132.53 (Ar CH); 131.26 (Ar CH); 129.45 (Ar CH); 129.41 (Ar CH); 123.94 (Ar CH); 118.72 (Ar q); 110.68 (Ar q); 57.15 (CH$_2$); 28.07 (CH$_2$)

HRMS (ESI): Calculated for [C$_{15}$H$_{13}$NOSNa]$^+$ (M+Na$^+$): 278.061005; found: 278.061040
1-Methyl-4-(2-(phenylsulfinyl)ethyl)benzene (1f)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 99 mg (81% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.61-7.59 (m, 2H); 7.51-7.46 (m, 3H); 7.08-7.03 (m, 4H); 3.06-2.95 (m, 3H); 2.84-2.80 (m, 1H); 2.28 (s, 3H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 143.70 (Ar q); 136.30 (Ar q); 135.64 (Ar q); 131.01 (Ar CH); 129.44 (Ar CH); 129.28 (Ar CH); 128.44 (Ar CH); 124.03 (Ar CH); 58.52 (CH$_2$); 27.79 (CH$_2$); 21.05 (CH$_3$)

HRMS (ESI): Calculated for [C$_{15}$H$_{16}$OSNa]$^+$ (M+Na$^+$): 267.081406; found: 267.081540

1-Methoxy-4-(2-(phenylsulfinyl)ethyl)benzene (1g)
Synthesized according to the general procedure, using a 6/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 124 mg (95% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.61-7.59 (m, 2H); 7.51-7.46 (m, 3H); 7.07-7.06 (m, 2H); 6.80-6.79 (m, 2H); 3.74 (s, 3H); 3.04-2.96 (m, 3H); 2.84-2.80 (m, 1H);

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 158.38 (Ar q); 143.71 (Ar q); 131.00 (Ar CH); 130.68 (Ar q); 129.56 (Ar CH); 129.28 (Ar CH); 124.00 (Ar CH); 114.15 (Ar CH); 58.68 (CH$_2$); 55.27 (OCH$_3$); 27.39 (CH$_2$)

HRMS (ESI): Calculated for [C$_{15}$H$_{16}$O$_2$SNa]$^+$ (M+Na$^+$): 283.076322; found: 283.076100

1-Bromo-2-(2-(phenylsulfinyl)ethyl)benzene (3)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 128 mg (83% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.63-7.61 (m, 2H); 7.53-7.47 (m, 4H); 7.25-7.19 (m, 2H); 7.08-7.04 (m, 1H); 3.20-3.13 (m, 1H); 3.00-2.95 (m, 2H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 143.33 (Ar q); 138.16 (Ar q); 133.06 (Ar CH); 131.05 (Ar CH); 130.92 (Ar CH); 129.26 (Ar CH); 128.58 (Ar CH); 127.85 (Ar CH); 124.33 (Ar q); 124.09 (Ar CH); 55.86 (CH$_2$); 28.70 (CH$_2$)

HRMS (ESI): Calculated for [C$_{14}$H$_{13}$BrOSNa]$^+$ (M+Na$^+$): 330.976282; found: 330.976470
1-Methyl-3-(2-(phenylsulfinyl)ethyl)benzene (4)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 110 mg (90% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.61-7.59 (m, 2H); 7.51-7.46 (m, 3H); 7.15-7.12 (m, 1H); 6.70-6.93 (m, 3H); 3.06-2.97 (m, 3H); 2.86-2.80 (m, 1H); 2.27 (s, 3H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 143.67 (Ar q); 138.69 (Ar q); 138.41 (Ar q); 131.03 (Ar CH); 129.36 (Ar CH); 129.28 (Ar CH); 128.65 (Ar CH); 127.45 (Ar CH); 125.55 (Ar CH); 124.03 (Ar CH); 58.38 (CH$_2$); 28.11 (CH$_2$); 21.38 (CH$_3$)

HRMS (ESI): Calculated for [C$_{15}$H$_{16}$OSNa]$^+$ (M+Na$^+$): 267.081407; found: 267.081500

1,3,5-Trimethyl-2-(2-(phenylsulfinyl)ethyl)benzene (5)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 129 mg (95% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.62-7.60 (m, 2H); 7.50-7.46 (m, 3H); 6.75 (s, 2H); 3.01-2.89 (m, 2H); 2.75-2.69 (m, 2H); 2.17 (s, 3H); 2.10 (s, 6H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 143.48 (Ar q); 136.18 (Ar q); 136.06 (Ar q); 132.25 (Ar q); 131.01 (Ar CH); 129.23 (Ar CH); 129.17 (Ar CH); 124.08 (Ar CH); 54.66 (CH$_2$); 20.93 (CH$_3$); 20.81 (CH$_2$); 19.48 (CH$_3$)

HRMS (ESI): Calculated for [C$_{17}$H$_{20}$OSNa]$^+$ (M+Na$^+$): 295.112706; found: 295.112500

2-(2-(Phenylsulfinyl)ethyl)naphthalene (6)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 92 mg (66% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.80-7.75 (m, 3H); 7.66-7.63 (m, 3H); 7.55-7.43 (m, 5H); 7.30-7.28 (m, 1H); 3.30-2.24 (m, 1H); 3.19-3.02 (m, 3H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 143.63 (Ar q); 136.20 (Ar q); 133.56 (Ar q); 132.27 (Ar q); 131.07 (Ar CH); 129.32 (Ar CH); 128.49 (Ar CH); 127.68 (Ar CH); 127.50 (Ar CH); 127.03 (Ar CH); 126.85 (Ar CH); 126.27 (Ar CH); 125.70 (Ar CH); 124.05 (Ar CH); 58.25 (CH$_2$); 28.33 (CH$_2$)

HRMS (ESI): Calculated for [C$_{18}$H$_{16}$OSNa]$^+$ (M+Na$^+$): 303.081407; found: 303.081420
((2-Phenylpropyl)sulfinyl)benzene (7)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 101 mg (83% yield) in a 1.8:1 dr as determined by NMR analysis.

\[ \begin{array}{c}
\text{Ph} \\
\text{S} \\
\text{Ph}
\end{array} \]

\[ ^1H \text{ NMR:} \quad (\text{CDCl}_3; 500 \text{ MHz, 2 diastereoisomers}): \quad 7.66-7.21 (\text{m, 10H}); \quad 3.45-3.41 (\text{m, 1H, major}); \quad 3.40-3.34 (\text{m, 1H, minor}); \quad 3.16-3.12 (\text{m, 1H, minor}); \quad 3.11-3.08 (\text{m, 1H, major}); \quad 2.96-2.91 (\text{m, 1H, major}); \quad 2.87-2.82 (\text{m, 1H, minor}); \quad 1.56 (d, J=6.9 \text{ Hz, 3H, minor}); \quad 1.43 (d, J=7.1 \text{ Hz, 3H, major})
\]

\[ ^13C \text{ NMR:} \quad (\text{CDCl}_3; 125 \text{ MHz, 2 diastereoisomers}): \quad 144.70 (\text{Ar q, major}); \quad 144.48 (\text{Ar q, minor}); \quad 144.23 (\text{Ar q, minor}); \quad 143.79 (\text{Ar q, major}); \quad 131.09 (\text{Ar CH, minor}); \quad 130.98 (\text{Ar CH, major}); \quad 129.31 (\text{Ar CH, minor}); \quad 129.28 (\text{Ar CH, major}); \quad 128.89 (\text{Ar CH, major}); \quad 128.78 (\text{Ar CH, minor}); \quad 127.22 (\text{Ar CH, major}); \quad 127.10 (\text{Ar CH, minor}); \quad 126.86 (\text{Ar CH, minor}); \quad 126.86 (\text{Ar CH, major}); \quad 124.00 (\text{Ar CH, minor}); \quad 123.85 (\text{Ar CH, major}); \quad 67.30 (\text{CH}_2, \text{ major}); \quad 66.66 (\text{CH}_2, \text{ minor}); \quad 34.41 (\text{CH, major}); \quad 34.57 (\text{CH, minor}); \quad 22.30 (\text{CH}_3, \text{ major}); \quad 20.63 (\text{CH}_3, \text{ minor})
\]

\[ \text{HRMS (ESI): Calculated for [C}_{15}\text{H}_{16}\text{OSNa}^+ (\text{M+Na}^+): 267.081407; found: 267.081510} \]

((1-Phenylpropan-2-yl)sulfinyl)benzene (8)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 29 mg (24% yield) in a 1.2:1 dr as determined by NMR analysis.

\[ \begin{array}{c}
\text{Ph} \\
\text{S} \\
\text{Ph}
\end{array} \]

\[ ^1H \text{ NMR:} \quad (\text{CDCl}_3; 500 \text{ MHz, 2 diastereoisomers}): \quad 7.67-7.08 (\text{m, 10H}); \quad 3.29 (dd, J=13.6 and 5.8 \text{ Hz, 1H, minor}); \quad 3.09 (dd, J=13.5 and 3.6 \text{ Hz, 1H, major}); \quad 2.96-2.87 (\text{m, 1H}); \quad 2.62-2.56 (\text{m, 1H}); \quad 1.09 (d, J=6.9 \text{ Hz, 3H, major}); \quad 0.99 (d, J=6.8 \text{ Hz, 3H, minor})
\]

\[ ^13C \text{ NMR:} \quad (\text{CDCl}_3; 125 \text{ MHz, 2 diastereoisomers}): \quad 141.73 (\text{Ar q, major}); \quad 141.55 (\text{Ar q, minor}); \quad 138.12 (\text{Ar q, minor}); \quad 137.73 (\text{Ar q, major}); \quad 131.24 (\text{Ar CH, minor}); \quad 130.83 (\text{Ar CH, major}); \quad 129.28 (\text{Ar CH, major}); \quad 129.25 (\text{Ar CH, minor}); \quad 129.08 (\text{Ar CH, major}); \quad 128.94 (\text{Ar CH, minor}); \quad 128.68 (\text{Ar CH, minor}); \quad 128.59 (\text{Ar CH, major}); \quad 126.75 (\text{Ar CH, minor}); \quad 126.63 (\text{Ar CH, major}); \quad 125.20 (\text{Ar CH, minor}); \quad 124.78 (\text{Ar CH, major}); \quad 60.95 (\text{CH}, \text{ major}); \quad 60.90 (\text{CH}, \text{ minor}); \quad 36.64 (\text{CH}_2, \text{ minor}); \quad 34.52 (\text{CH}_2, \text{ major}); \quad 12.75 (\text{CH}_3, \text{ major}); \quad 10.26 (\text{CH}_3, \text{ minor})
\]

\[ \text{HRMS (ESI): Calculated for [C}_{15}\text{H}_{16}\text{OSNa}^+ (\text{M+Na}^+): 267.081407; found: 267.081420} \]

2-(2-(Phenylsulfinyl)ethyl)naphthalene (9)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 57 mg (37% yield).
$^1$H NMR: (CDCl$_3$; 500 MHz): 7.61-7.59 (m, 2H); 7.50-7.48 (m, 3H); 7.37-7.32 (m, 4H); 7.28-7.17 (m, 6H); 4.58 (dd, J=10.8 and 5.2 Hz, 1H); 3.49-3.45 (m, 1H); 3.42-3.37 (m, 1H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 143.35 (Ar q); 142.34 (Ar q); 141.31 (Ar q); 131.20 (Ar CH); 129.35 (Ar CH); 128.95 (Ar CH); 128.76 (Ar CH); 128.25 (Ar CH); 127.69 (Ar CH); 127.25 (Ar CH); 126.94 (Ar CH); 124.04 (Ar CH); 64.75 (CH$_2$); 45.43 (CH$_2$)

HRMS (ESI): Calculated for [C$_{20}$H$_{18}$OSNa]$^+$ (M+Na$^+$): 329.097056; found: 329.096910

2-(Phenylsulfinyl)-2,3-dihydro-1H-indene (10)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 57 mg (47% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.69-7.67 (m, 2H); 7.53-7.50 (m, 3H); 7.17-7.13 (m, 4H); 3.68-3.62 (m, 1H); 3.55-3.50 (m, 1H); 3.20-3.06 (m, 2H); 3.02-2.97 (m, 1H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 143.09 (Ar q); 140.47 (Ar q); 140.28 (Ar q); 131.30 (Ar CH); 129.20 (Ar CH); 127.07 (Ar CH); 126.91 (Ar CH); 124.79 (Ar CH); 124.70 (Ar CH); 124.38 (Ar CH); 63.85 (CH); 33.52 (CH$_2$); 31.84 (CH$_2$)

HRMS (ESI): Calculated for [C$_{15}$H$_{14}$OSNa]$^+$ (M+Na$^+$): 265.065757; found: 265.065800

2-(Phenylsulfinyl)-1,2,3,4-tetrahydronaphthalene (11)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 72 mg (56% yield) in a 1.5:1 dr as determined by NMR analysis.

$^1$H NMR: (CDCl$_3$; 500 MHz, 2 diastereoisomers): 7.67-7.63 (m, 2H); 7.54-7.51 (m, 3H); 7.11-6.70 (m, 4H); 3.09-1.81 (m, 7H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz, 2 diastereoisomers): 141.73 (Ar q, major); 141.70 (Ar q, minor); 135.66 (Ar q, major); 135.34 (Ar q, minor); 133.98 (Ar CH, minor); 133.55 (Ar CH, major); 131.43 (Ar CH, major); 131.17 (Ar CH, minor); 129.40 (Ar CH, minor); 129.19 (Ar CH, major); 129.13 (Ar CH, major); 129.06 (Ar CH, minor); 128.87 (Ar CH, major); 128.66 (Ar CH, minor); 126.39 (Ar CH, major 126.21 (Ar CH, minor); 126.15 (Ar CH, minor); 125.22 (Ar CH, major); 124.88 (Ar CH, minor); 60.58 (CH, major); 59.77 (CH, minor); 28.98 (CH$_2$, major); 28.67 (CH$_2$, minor); 28.14 (CH$_2$, major); 26.14 (CH$_2$, minor); 23.71 (CH$_2$, minor); 21.84 (CH$_2$, major)

HRMS (ESI): Calculated for [C$_{16}$H$_{16}$OSNa]$^+$ (M+Na$^+$): 279.081407; found: 279.081450
(Cyclohexylsulfinyl)benzene (12)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 5 mg (5% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.60-7.58 (m, 2H); 7.52-7.48 (m, 3H); 2.59-2.53 (m, 1H); 1.84-1.81 (m, 4H); 1.65-1.63 (m, 1H); 1.48-1.35 (m, 2H); 1.29-1.16 (m, 3H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 141.88 (Ar q); 130.93 (Ar CH); 128.91 (Ar CH); 125.03 (Ar CH); 63.16 (CH); 26.28 (CH$_2$); 25.62 (CH$_2$); 25.46 (CH$_2$); 25.33 (CH$_2$); 24.02 (CH$_2$)

HRMS (ESI): Calculated for [C$_{12}$H$_{16}$OSNa$^+$] (M+Na$^+$): 231.081407; found: 231.081290

(Cyclopent-2-en-1-ylsulfinyl)benzene (13)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 38 mg (40% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.64-7.62 (m, 2H); 7.48-7.46 (m, 3H); 5.67-5.65 (m, 1H); 5.62-5.60 (m, 1H); 3.48-3.42 (m, 1H); 2.92-2.86 (m, 1H); 2.57-2.53 (m, 2H); 2.45-2.40 (m, 1H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 144.33 (Ar q); 131.11 (Ar CH); 129.27 (CH); 129.10 (Ar CH); 128.54 (CH); 124.82 (Ar CH); 62.09 (CH); 33.74 (CH$_2$); 31.86 (CH$_2$)

HRMS (ESI): Calculated for [C$_{11}$H$_{13}$OSNa$^+$] (M+Na$^+$): 193.068163; found: 193.068360

(Octylsulfinyl)benzene (14)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 15 mg (13% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.60-7.58 (m, 2H); 7.50-7.46 (m, 3H); 2.77-2.73 (m, 2H); 1.74-1.67 (m, 1H); 1.62-1.55 (m, 1H); 1.41-1.33 (m, 2H); 1.25-1.21 (m, 8H); 0.83 (d, J=7.0 Hz, 3H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 144.06 (Ar q); 130.91 (Ar CH); 129.19 (Ar CH); 124.04 (Ar CH); 57.40 (CH$_2$); 31.72 (CH$_2$); 29.13 (CH$_2$); 29.09 (CH$_2$); 28.68 (CH$_2$); 22.60 (CH$_2$); 22.18 (CH$_2$); 14.08 (CH$_3$)

HRMS (ESI): Calculated for [C$_{14}$H$_{23}$OSNa$^+$] (M+Na$^+$): 239.146413; found: 239.146440
Methyl 3-(phenylsulfinyl)propanoate (15a)
Synthesized according to the general procedure, using a 6/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 15 mg (14% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.62-7.60 (m, 2H); 7.54-7.49 (m, 3H); 3.65 (s, 3H); 3.25-3.20 (m, 1H); 2.98-2.92 (m, 1H); 2.86-2.80 (m, 1H); 2.57-2.51 (m, 1H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 171.69 (C); 142.88 (Ar q); 131.20 (Ar CH); 129.33 (Ar CH); 124.03 (Ar CH); 51.16 (CH$_3$); 51.09 (CH$_2$); 25.94 (CH$_2$)

HRMS (ESI): Calculated for [C$_{10}$H$_{13}$O$_3$SNa]$^+$ (M+Na$^+$): 213.057993; found: 213.058030

Ethyl 3-(phenylsulfinyl)propanoate (15b)
Synthesized according to the general procedure, using a 6/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 59 mg (52% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.60-7.58 (m, 2H); 7.52-7.47 (m, 3H); 4.10-4.06 (m, 2H); 3.23-3.17 (m, 1H); 2.96-2.91 (m, 1H); 2.83-2.77 (m, 1H); 2.54-2.47 (m, 1H); 1.21 (d, J=7.1 Hz, 3H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 171.22 (C); 142.93 (Ar q); 131.17 (Ar CH); 129.32 (Ar CH); 124.03 (Ar CH); 61.15 (CH$_2$); 51.17 (CH$_2$); 26.18 (CH$_2$); 14.13 (CH$_3$)

HRMS (ESI): Calculated for [C$_{11}$H$_{14}$O$_3$SNa]$^+$ (M+Na$^+$): 249.055587; found: 249.055570

Butyl 3-(phenylsulfinyl)propanoate (15c)
Synthesized according to the general procedure, only with 3.0 equivalents of thiophenol, and using a 6/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 88 mg (69% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.59-7.57 (m, 2H); 7.49-7.47 (m, 3H); 4.07-4.00 (m, 2H); 3.22-3.16 (m, 1H); 2.95-2.90 (m, 1H); 2.83-2.76 (m, 1H); 2.52-2.46 (m, 1H); 1.56-1.51 (m, 2H); 1.34-1.29 (m, 2H); 0.88 (d, J=7.4 Hz, 3H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 171.30 (C); 142.94 (Ar q); 131.16 (Ar CH); 129.31 (Ar CH); 124.02 (Ar CH); 65.04 (CH$_2$); 51.19 (CH$_2$); 30.52 (CH$_2$); 26.15 (CH$_2$); 19.07 (CH$_2$); 13.67 (CH$_3$)

HRMS (ESI): Calculated for [C$_{13}$H$_{18}$O$_3$SNa]$^+$ (M+Na$^+$): 277.086887; found: 277.086900
tert-Butyl 3-(phenylsulfinyl)propanoate (15d)
Synthesized according to the general procedure, only with 3.0 equivalents of thiophenol, and a 6/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 70 mg (54% yield).

\[ ^1H \text{ NMR: (CDCl}_3; 500 MHz): 7.62-7.60 \text{ (m, 2H); 7.53-7.48 \text{ (m, 3H); 3.19-3.13 \text{ (m, 1H); 2.94-2.89 \text{ (m, 1H); 2.78-2.71 \text{ (m, 1H); 2.46-2.40 \text{ (m, 1H); 1.40 (s, 9H)}}} \]

\[ ^13C \text{ NMR: (CDCl}_3; 125 MHz): 170.38 \text{ (C); 143.12 \text{ (Ar q); 131.10 \text{ (Ar CH)); 129.30 \text{ (Ar CH); 124.02 \text{ (Ar CH); 81.54 \text{ (C); 51.51 \text{ (CH}_2)); 28.02 \text{ (CH}_3)); 27.33 \text{ (CH}_2)} \]

HRMS (ESI): Calculated for \([\text{C}_{13}\text{H}_{18}\text{O}_3\text{SNa}]^+ \text{ (M+Na}^+\): 277.086887; found: 277.086890

Benzyl 3-(phenylsulfinyl)propanoate (15e)
Synthesized according to the general procedure, only with 3.0 equivalents of thiophenol, and a 6/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 104 mg (72% yield).

\[ ^1H \text{ NMR: (CDCl}_3; 500 MHz): 7.62-7.61 \text{ (m, 2H); 7.53-7.51 \text{ (m, 3H); 7.36-7.33 \text{ (m, 5H); 5.10 (s, 2H); 3.29-3.24 \text{ (m, 1H); 3.02-2.96 \text{ (m, 1H); 2.93-2.87 \text{ (m, 1H); 2.62-2.56 \text{ (m, 1H)}}} \]

\[ ^13C \text{ NMR: (CDCl}_3; 125 MHz): 171.06 \text{ (C); 142.82 \text{ (Ar q); 135.39 \text{ (Ar q); 131.20 \text{ (Ar CH); 129.34 \text{ (Ar CH); 128.64 \text{ (Ar CH); 128.48 \text{ (Ar CH); 128.37 \text{ (Ar CH); 124.03 \text{ (Ar CH); 66.95 \text{ (CH}_2); 50.99 \text{ (CH}_2); 26.11 \text{ (CH}_2)} \]

HRMS (ESI): Calculated for \([\text{C}_{16}\text{H}_{16}\text{O}_3\text{SNa}]^+ \text{ (M+Na}^+\): 311.071237; found: 311.071240

3-(Phenylsulfinyl)propanenitrile (16)
Synthesized according to the general procedure, using a 6/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 16 mg (18% yield).

\[ ^1H \text{ NMR: (CDCl}_3; 500 MHz): 7.55-7.50 \text{ (m, 5H); 3.20-3.14 \text{ (m, 1H); 2.89-2.79 \text{ (m, 2H); 2.46-2.40 \text{ (m, 1H)}}} \]

\[ ^13C \text{ NMR: (CDCl}_3; 125 MHz): 141.35 \text{ (Ar q); 131.82 \text{ (Ar CH); 129.69 \text{ (Ar CH); 123.93 \text{ (Ar CH); 117.24 \text{ (C); 50.27 \text{ (CH}_2); 9.53 \text{ (CH}_2)} \]

HRMS (ESI): Calculated for \([\text{C}_9\text{H}_9\text{OSNa}]^+ \text{ (M+Na}^+\): 202.029705; found: 202.029730

N,N-Dimethyl-3-(phenylsulfinyl)propanamide (17)
Synthesized according to the general procedure, using a 3/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 87 mg (77% yield).
**N,N,2-Trimethyl-3-(phenylsulfinyl)propanamide (18)**

Synthesized according to the general procedure, using a 3/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 10 mg (8% yield) in a 1.2:1 dr as determined by NMR analysis.

**1H NMR:** (CDCl₃; 500 MHz, 2 diastereoisomers): 7.64-7.44 (m, 5H); 3.44-3.41 (m, 1H, minor); 3.36-3.30 (m, 1H, minor); 3.36-3.30 (m, 1H, major); 3.20-3.16 (m, 1H, major); 3.13 (s, 3H, minor); 3.00 (s, 3H, minor); 2.97 (s, 3H, major); 2.84-2.79 (m, 1H, major); 2.76 (s, 3H, major); 2.69-2.64 (m, 1H, minor); 1.32 (d, J=6.9 Hz, 3H, major); 1.17 (d, J=7.0 Hz, 3H, minor)

**13C NMR:** (CDCl₃; 125 MHz, 2 diastereoisomers): 173.67 (C, minor); 173.61 (C, major); 144.65 (Ar q, minor); 143.28 (Ar q, major); 130.94 (Ar CH, minor); 130.83 (Ar CH, major); 129.22 (Ar CH, minor); 129.10 (Ar CH, major); 123.99 (Ar CH, major); 123.67 (Ar CH, minor); 61.87 (CH₂, minor); 60.85 (CH₂, major); 37.30 (CH₃, minor); 37.13 (CH₃, major); 35.88 (CH₃, minor); 35.64 (CH₃, major); 31.29 (CH₃, minor); 29.72 (CH₃, major); 17.98 (CH₃, minor); 17.09 (CH₃, major)

**HRMS (ESI):** Calculated for [C₁₂H₁₈NO₂S]⁺ (M+H⁺): 240.105276; found: 240.105270

**N-Methyl-N-phenyl-3-(phenylsulfinyl)propanamide (19)**

Synthesized according to the general procedure, using a 5/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 103 mg (72% yield).

**1H NMR:** (CDCl₃; 500 MHz): 7.50-7.48 (m, 2H); 7.41-7.40 (m, 3H); 7.35 (t, J=7.8 Hz, 2H); 7.29 (t, J=7.4 Hz, 1H); 7.09 (d, J=7.2 Hz, 2H); 3.18 (s, 3H); 3.16-3.12 (m, 1H); 2.86-2.81 (m, 1H); 2.58-2.52 (m, 1H); 2.32-2.26 (m, 1H)

**13C NMR:** (CDCl₃; 125 MHz): 170.02 (C); 143.67 (Ar q); 143.14 (Ar q); 130.94 (Ar CH); 130.04 (Ar CH); 129.17 (Ar CH); 128.23 (Ar CH); 127.20 (Ar CH); 123.92 (Ar CH); 52.81 (CH₂); 37.46 (CH₃); 27.14 (CH₂)

**HRMS (ESI):** Calculated for [C₁₆H₁₈NO₂S]⁺ (M+H⁺): 288.105276; found: 288.105080
N-phenyl-3-(phenylsulfinyl)propanamide (20)
Synthesized according to the general procedure, only with 3.0 equivalents of thiophenol, and using a 2/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 97 mg (71% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 9.08 (s, 1H); 7.58-7.56 (m, 2H); 7.46-7.44 (m, 5H); 7.18 (t, J=7.9 Hz, 2H); 6.98 (t, J=7.4 Hz, 1H); 3.37-3.32 (m, 1H); 3.04-2.91 (m, 2H); 2.74-2.68 (m, 1H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 168.51 (C); 142.33 (Ar q); 138.30 (Ar q); 131.30 (Ar CH); 129.49 (Ar CH); 128.87 (Ar CH); 124.10 (Ar CH); 123.99 (Ar CH); 119.82 (Ar CH); 51.90 (CH$_2$); 29.49 (CH$_2$)

HRMS (ESI): Calculated for [C$_{15}$H$_{15}$NO$_2$SNa]$^+$ (M+Na$^+$): 296.071570; found: 296.071670

2-Methyl-N-phenyl-3-(phenylsulfinyl)propanamide (21)
Synthesized according to the general procedure, only with 4.0 equivalents of thiophenol, and a 2/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 115 mg (80% yield) in a 1.1:1 dr as determined by NMR analysis.

$^1$H NMR: (CDCl$_3$; 500 MHz, 2 diastereoisomers): 8.97 (s, 1H, minor); 8.97 (s, 1H, major); 7.59-6.97 (m, 10H); 3.38-2.67 (m, 3H); 1.43 (d, J=6.9 Hz, 3H, minor); 1.21 (d, J=7.0 Hz, 3H, major)

$^{13}$C NMR: (CDCl$_3$; 125 MHz, 2 diastereoisomers): 172.17 (C, minor); 172.02 (C, major); 142.99 (Ar q, minor); 142.63 (Ar q, major); 138.36 (Ar q, major); 138.30 (Ar q, minor); 131.41 (Ar CH, minor); 131.31 (Ar CH, major); 129.47 (Ar CH, minor); 129.46 (Ar CH, major); 128.92 (Ar CH, minor); 128.80 (Ar CH, major); 124.20 (Ar CH, minor); 123.99 (Ar CH, major); 123.93 (Ar CH, major); 123.85 (Ar CH, minor); 119.96 (Ar CH, major); 119.69 (Ar CH, minor); 61.22 (CH$_2$, minor); 50.82 (CH$_2$, major); 36.33 (CH, major); 35.91 (CH, minor); 18.75 (CH$_3$, minor); 17.49 (CH$_3$, major)

HRMS (ESI): Calculated for [C$_{16}$H$_{17}$NO$_2$SNa]$^+$ (M+Na$^+$): 310.087220; found: 310.087280

3-(Phenylsulfinyl)propanamide (22)
Synthesized according to the general procedure, using a 1/2 mixture of hexane and acetone for column chromatography, isolated as a white solid, 65 mg (71% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.61-7.59 (m, 2H); 7.54-7.50 (m, 3H); 6.33 (s, 1H); 5.61 (s, 1H); 3.31-3.25 (m, 1H); 2.98-2.93 (m, 1H); 2.82-2.76 (m, 1H); 2.54-2.48 (m, 1H)
**13C NMR:** (CDCl₃; 125 MHz): 172.31 (C); 142.88 (Ar q); 131.20 (Ar CH); 129.35 (Ar CH); 123.97 (Ar CH); 51.62 (CH₂); 27.76 (CH₂)

**HRMS (ESI):** Calculated for [C₉H₁₁NO₂SNa⁺]⁺ (M+Na⁺): 220.040270; found: 220.040300

![1-Fluoro-4-(phenethylsulfinyl)benzene (23)](image)

1-Fluoro-4-(phenethylsulfinyl)benzene (23)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as clear oil, 123 mg (99% yield).

**1H NMR:** (CDCl₃; 500 MHz): 7.67-7.64 (m, 2H); 7.32-7.29 (m, 2H); 7.26-7.22 (m, 3H); 7.20-7.19 (m, 2H); 3.16-3.01 (m, 3H); 2.94-2.88 (m, 1H)

**13C NMR:** (CDCl₃; 125 MHz): 164.34 (d, J=251.3 Hz, Ar q); 139.07 (d, J=3.1 Hz, Ar q); 138.55 (Ar q); 126.80 (Ar CH); 126.80 (Ar CH); 126.33 (d, J=8.6 Hz, Ar CH); 116.65 (d, J=22.47 Hz, Ar CH); 58.54 (CH₂); 28.18 (CH₂)

**HRMS (ESI):** Calculated for [C₁₄H₁₃OFSNa⁺]⁺ (M+Na⁺): 271.056335; found: 271.056270

![1-Chloro-4-(phenethylsulfinyl)benzene (24)](image)

1-Chloro-4-(phenethylsulfinyl)benzene (24)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 119 mg (90% yield).

**1H NMR:** (CDCl₃; 500 MHz): 7.57-7.55 (m, 2H); 7.50-7.48 (m, 2H); 7.30-7.26 (m, 2H); 7.23-7.21 (m, 1H); 7.17-7.16 (m, 2H); 3.12-2.97 (m, 3H); 2.90-2.84 (m, 1H)

**13C NMR:** (CDCl₃; 125 MHz): 142.16 (Ar q); 138.48 (Ar q); 137.27 (Ar q); 129.59 (Ar CH); 128.81 (Ar CH); 128.55 (Ar CH); 126.82 (Ar CH); 125.47 (Ar CH); 58.36 (CH₂); 28.07 (CH₂)

**HRMS (ESI):** Calculated for [C₁₄H₁₃OCISNa⁺]⁺ (M+Na⁺): 287.026785; found: 287.026870

![1-Bromo-4-(phenethylsulfinyl)benzene (25)](image)

1-Bromo-4-(phenethylsulfinyl)benzene (25)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 141 mg (91% yield).

**1H NMR:** (CDCl₃; 500 MHz): 7.67-7.65 (m, 2H); 7.50-7.49 (m, 2H); 7.30-7.22 (m, 3H); 7.18-7.16 (m, 2H); 3.13-2.97 (m, 3H); 2.90-2.84 (m, 1H)

**13C NMR:** (CDCl₃; 125 MHz): 142.79 (Ar q); 138.47 (Ar q); 132.51 (Ar CH); 128.82 (Ar CH); 128.55 (Ar CH); 126.82 (Ar CH); 125.48 (Ar q); 58.30 (CH₂); 28.05 (CH₂)

**HRMS (ESI):** Calculated for [C₁₄H₁₃OBrSNa⁺]⁺ (M+Na⁺): 330.976282; found: 330.976370
1-Methyl-4-(phenethylsulfinyl)benzene (26)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 113 mg (93% yield).

\(^1\)H NMR: (CDCl\(_3\); 500 MHz): 7.55-7.54 (m, 2H); 7.36-7.34 (m, 2H); 7.32-7.29 (m, 2H); 7.25-7.19 (m, 3H); 3.13-3.03 (m, 3H); 2.93-2.88 (m, 1H); 2.44 (s, 3H)
\(^{13}\)C NMR: (CDCl\(_3\); 125 MHz): 141.53 (Ar q); 140.34 (Ar q); 138.85 (Ar q); 129.99 (Ar CH); 128.74 (Ar CH); 128.55 (Ar CH); 126.67 (Ar CH); 124.08 (Ar CH); 58.35 (CH\(_2\)); 28.21 (CH\(_2\)); 21.44 (CH\(_3\))
HRMS (ESI): Calculated for [C\(_{15}\)H\(_{16}\)OSNa\(^+\)] (M+Na\(^+\)): 267.081407; found: 267.081350

1-Methyl-2-(phenethylsulfinyl)benzene (27)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 112 mg (92% yield).

\(^1\)H NMR: (CDCl\(_3\); 500 MHz): 7.94-7.92 (m, 1H); 7.44-7.41 (m, 1H); 7.39-7.35 (m, 1H); 7.29-7.26 (m, 2H); 7.22-7.18 (m, 4H); 3.13-3.03 (m, 2H); 2.98-2.92 (m, 2H); 2.30 (s, 3H)
\(^{13}\)C NMR: (CDCl\(_3\); 125 MHz): 141.85 (Ar q); 138.89 (Ar q); 134.27 (Ar q); 130.76 (Ar CH); 128.75 (Ar CH); 128.55 (Ar CH); 127.19 (Ar CH); 126.70 (Ar CH); 123.92 (Ar CH); 56.37 (CH\(_2\)); 28.48 (CH\(_2\)); 18.15 (CH\(_3\))
HRMS (ESI): Calculated for [C\(_{15}\)H\(_{16}\)OSNa\(^+\)] (M+Na\(^+\)): 267.081407; found: 267.081320

1-Methyl-3-(phenethylsulfinyl)benzene (28)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 112 mg (92% yield).

\(^1\)H NMR: (CDCl\(_3\); 500 MHz): 7.47-7.46 (m, 1H); 7.40-7.38 (m, 2H); 7.30-7.27 (m, 3H); 7.29-7.26 (m, 3H); 7.22-7.17 (m, 3H); 3.09-3.01 (m, 3H); 2.93-2.88 (m, 1H); 2.42 (s, 3H)
\(^{13}\)C NMR: (CDCl\(_3\); 125 MHz): 143.47 (Ar q); 139.54 (Ar q); 138.84 (Ar q); 131.86 (Ar CH); 129.08 (Ar CH); 128.74 (Ar CH); 128.57 (Ar CH); 126.69 (Ar CH); 124.30 (Ar CH); 121.13 (Ar CH); 58.33 (CH\(_2\)); 28.27 (CH\(_2\)); 21.46 (CH\(_3\))
HRMS (ESI): Calculated for [C\(_{15}\)H\(_{16}\)OSNa\(^+\)] (M+Na\(^+\)): 267.081407; found: 267.081370
2-(Phenethylsulfinyl)naphthalene (29)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 130 mg (93% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 8.23 (s, 1H); 8.01-7.92 (m, 3H); 7.63-7.59 (m, 3H); 7.32-7.29 (m, 2H); 7.25-7.19 (m, 3H); 3.22-3.12 (m, 3H); 2.96-2.90 (m, 1H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 140.59 (Ar q); 138.75 (Ar q); 134.44 (Ar q); 132.90 (Ar q); 129.53 (Ar CH); 128.76 (Ar CH); 128.59 (Ar CH); 128.51 (Ar CH); 128.10 (Ar CH); 127.82 (Ar CH); 127.39 (Ar CH); 126.73 (Ar CH); 124.82 (Ar CH); 119.81 (Ar CH); 57.91 (CH$_2$); 28.14 (CH$_2$)

HRMS (ESI): Calculated for [C$_{18}$H$_{16}$OSNa]$^+$ (M+Na$^+$): 303.081406; found: 303.081600

(2-(Benzylsulfinyl)ethyl)benzene (30)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 21 mg (17% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.28-7.11 (m, 10H); 3.98 (d, J=12.9 Hz, 1H); 3.88 (d, J=12.9 Hz, 1H); 3.06-3.01 (m, 1H); 2.97-2.91 (m, 1H); 2.78-2.75 (m, 2H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 138.87 (Ar q); 130.02 (Ar CH); 129.76 (Ar q); 129.04 (Ar CH); 128.79 (Ar CH); 128.60 (Ar CH); 128.44 (Ar CH); 126.78 (Ar CH); 58.38 (CH$_2$); 52.20 (CH$_2$); 28.65 (CH$_2$)

HRMS (ESI): Calculated for [C$_{15}$H$_{16}$OSNa]$^+$ (M+Na$^+$): 267.081407; found: 267.081420

(2-(tert-Butylsulfinyl)ethyl)benzene (31)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 16 mg (15% yield).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.33-7.31 (m, 2H); 7.28-7.23 (m, 3H); 3.24-3.18 (m, 1H); 3.07-3.01 (m, 1H); 2.77-2.66 (m, 2H); 1.24 (s, 9H)

$^{13}$C NMR: (CDCl$_3$; 125 MHz): 139.46 (Ar q); 128.76 (Ar CH); 128.67 (Ar CH); 126.71 (Ar CH); 126.53 (Ar CH); 53.03 (CH$_2$); 47.27 (C); 30.01 (CH$_2$); 22.89 (CH$_3$)

HRMS (ESI): Calculated for [C$_{12}$H$_{18}$OSNa]$^+$ (M+Na$^+$): 233.097057; found: 233.097110

(2-(Cyclohexylsulfinyl)ethyl)benzene (32)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 9 mg (8% yield).
**1H NMR:** (CDCl₃; 500 MHz): 7.33-7.30 (m, 2H); 7.25-7.22 (m, 3H); 3.18-3.12 (m, 1H); 3.09-3.03 (m, 1H); 2.94-2.83 (m, 2H); 2.59-2.53 (m, 1H); 2.14-2.11 (m, 1H); 1.93-1.90 (m, 3H); 1.71-1.24 (m, 6H)

**13C NMR:** (CDCl₃; 125 MHz): 139.27 (Ar q); 128.77 (Ar CH); 128.61 (Ar CH); 126.72 (Ar CH); 59.23 (CH₂); 50.41 (CH); 29.04 (CH₂); 26.36 (CH₂); 25.53 (CH₂); 25.43 (CH₂); 25.19 (CH₂); 25.05 (CH₂)

**HRMS (ESI):** Calculated for [C₁₄H₂₀OSNa]+ (M+Na⁺): 259.112707; found: 259.112760

(4-(Benzylsulfinyl)butyl)benzene (33)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 12 mg (9% yield).

**1H NMR:** (CDCl₃; 500 MHz): 7.36-7.31 (m, 3H); 7.26-7.23 (m, 4H); 7.18-7.15 (m, 1H); 7.12-7.11 (m, 2H); 4.01-3.87 (m, 2H); 2.62-2.59 (m, 2H); 2.55-2.52 (m, 2H); 1.81-1.65 (m, 4H)

**13C NMR:** (CDCl₃; 125 MHz): 141.57 (Ar q); 129.98 (Ar CH); 129.87 (Ar q); 129.00 (Ar CH); 128.42 (Ar CH); 128.38 (Ar CH); 128.36 (Ar CH); 125.98 (Ar CH); 58.34 (CH₂); 50.74 (CH₂); 35.46 (CH₂); 30.57 (CH₂); 22.09 (CH₂)

**HRMS (ESI):** Calculated for [C₁₇H₂₀OSNa]+ (M+Na⁺): 295.112870; found: 295.112870

(4-(tert-Butylsulfinyl)butyl)benzene (34)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 14 mg (12% yield).

**1H NMR:** (CDCl₃; 500 MHz): 7.29-7.26 (m, 2H); 7.20-7.17 (m, 3H); 2.69-2.66 (m, 2H); 2.46-2.43 (m, 2H); 1.93-1.74 (m, 4H); 1.80 (s, 9H)

**13C NMR:** (CDCl₃; 125 MHz): 151.64 (Ar q); 141.81 (Ar CH); 128.41 (Ar CH); 125.92 (Ar CH); 52.74 (CH₂); 45.54 (C); 35.64 (CH₂); 30.57 (CH₂); 23.50 (CH₂); 22.88 (CH₃)

**HRMS (ESI):** Calculated for [C₁₄H₂₂OSNa]+ (M+Na⁺): 261.128357; found: 261.128350

(2-(Phenylsulfinyl)vinyl)benzene (35)
Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 93 mg (82% yield) in a 1.3:1 E/Z as determined by NMR analysis of the crude reaction product. The E and Z isomers of 36 could also be separated by column chromatography using the same conditions.
**E-Isomer**

**1H NMR:** (CDCl$_3$; 500 MHz, E-29): 7.69-7.67 (m, 2H); 7.53-7.48 (m, 3H); 7.45-7.43 (m, 2H); 7.37 (d, J=15.7 Hz, 1H); 6.83 (d, J=15.4 Hz, 1H)

**13C NMR:** (CDCl$_3$; 125 MHz, E-29): 143.90 (Ar q); 136.46 (Ar CH); 133.71 (Ar q); 132.92 (Ar CH); 131.21 (Ar CH); 129.93 (Ar CH); 129.50 (Ar CH); 128.94 (Ar CH); 127.82 (Ar CH); 124.76 (Ar CH)

**HRMS (ESI):** Calculated for [C$_{14}$H$_{13}$OS]$^+$ (M+H$^+$): 229.068163; found: 229.068109

**Z-Isomer**

**1H NMR:** (CDCl$_3$; 500 MHz, Z-29): 7.68-7.66 (m, 2H); 7.60-7.58 (m, 2H); 7.53-7.48 (m, 3H); 7.13 (d, J=10.5 Hz, 1H); 6.44 (d, J=10.6 Hz, 1H)

**13C NMR:** (CDCl$_3$; 125 MHz, Z-29): 144.55 (Ar q); 138.99 (Ar CH); 136.69 (Ar CH); 133.78 (Ar q); 130.93 (Ar CH); 129.82 (Ar CH); 129.62 (Ar CH); 129.42 (Ar CH); 128.74 (Ar CH); 124.34 (Ar CH)

**HRMS (ESI):** Calculated for [C$_{14}$H$_{13}$OS]$^+$ (M+H$^+$): 229.068163; found: 229.068190

(2-(Phenylsulfinyl)vinyl)benzene (36)

Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a clear oil, 48mg (40% yield) in a 4.9:1 E/Z as determined by NMR analysis.

**1H NMR:** (CDCl$_3$; 500 MHz, E/Z): 7.67-7.03 (m, 10H); 1:90 (d, J=1:45 Hz, 3H, E); 1:89 (d, J=1:50 Hz, 3H, Z)

**13C NMR:** (CDCl$_3$; 125 MHz, E/Z): 142.86 (Ar q, major); 142.72 (Ar q, minor); 142.30 (Ar q, minor); 142.24 (Ar q, major); 136.97 (Ar CH, minor); 142.30 (Ar q, minor); 142.47 (Ar CH, major); 131.10 (Ar CH, major); 130.35 (Ar CH, minor); 129.50 (Ar CH, minor); 129.41 (Ar CH, major); 129.21 (Ar CH, major); 129.08 (Ar CH, minor); 128.65 (Ar CH, major); 128.60 (Ar CH, major); 128.56 (Ar CH, minor); 128.49 (Ar CH, minor); 125.19 (Ar CH, major); 124.36 (Ar CH, minor); 13.46 (CH$_3$, minor); 10.46 (CH$_3$, major)

**HRMS (ESI):** Calculated for [C$_{15}$H$_{14}$OSNa]$^+$ (M+Na$^+$): 265.065757; found: 265.065820

(2-(Phenylsulfinyl)vinyl)benzene (37)

Synthesized according to the general procedure, using a 8/1 mixture of hexane and acetone for column chromatography, isolated as a white solid, 62mg (41% yield). The ratio of the E/Z isomers could not be determined by NMR analysis, as the isomers were not distinguishable.

**1H NMR:** (CDCl$_3$; 500 MHz, E/Z): 7.60-6.81 (m, 16H)

**13C NMR:** (CDCl$_3$; 125 MHz, E/Z): 145.53; 142.55; 142.51; 139.67; 133.87; 131.88; 131.13; 130.26; 129.98; 129.82; 129.77; 129.62; 129.27; 129.04; 128.85; 128.83; 128.78; 128.75; 128.71; 128.65; 128.41; 127.74; 125.36; 124.55

**HRMS (ESI):** Calculated for [C$_{20}$H$_{16}$OSNa]$^+$ (M+Na$^+$): 327.081406; found: 327.081550
Phenethyl(phenyl)sulfane (2a)
Isolated as a byproduct from reactions between thiophenol and styrene under standard reaction conditions, or in higher amounts under different conditions, as indicated in Tables S1-S3.

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.38-7.36 (m, 2H); 7.33-7.29 (m, 4H); 7.26-7.20 (m, 4H); 3.20-3.17 (m, 2H); 2.96-2.92 (m, 2H)
$^{13}$C NMR: (CDCl$_3$; 125 MHz): 140.24 (Ar q); 136.37 (Ar q); 129.24 (Ar CH); 128.96 (Ar CH); 128.54 (Ar CH); 126.48 (Ar CH); 126.01 (Ar CH); 35.67 (CH$_2$); 35.13 (CH$_2$)
HRMS (ESI): Calculated for [C$_{14}$H$_{14}$S]$^+$ (M$^+$): 214:081623; found: 214:081753

(Phenethylsulfonyl)benzene (44a)
Isolated as a byproduct from reactions between thiophenol and styrene at elevated temperatures (See Table S3).

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.96-7.93 (m, 2H); 7.69-7.65 (m, 1H); 7.60-7.56 (m, 2H); 7.28-7.25 (m, 2H); 7.22-7.18 (m, 1H); 7.12-7.10 (m, 2H); 3.38-3.35 (m, 2H); 3.07-3.03 (m, 2H)
$^{13}$C NMR: (CDCl$_3$; 125 MHz): 139.00 (Ar q); 137.45 (Ar q); 133.85 (Ar CH); 129.39 (Ar CH); 128.84 (Ar CH); 128.31 (Ar CH); 128.10 (Ar CH); 126.96 (Ar CH); 57.54 (CH$_2$); 28.74 (CH$_2$)
HRMS (ESI): Calculated for [C$_{14}$H$_{14}$O$_2$SNa]$^+$ (M$^+$Na$^+$): 269.060672; found: 269.060730

2,2,6,6-Tetramethyl-1-(1-phenyl-2-(phenylthio)ethoxy)piperidine (38)

$^1$H NMR: (CDCl$_3$; 500 MHz): 7.26-7.04 (m, 10H); 4.74 (dd, J=9.8 and 4.0 Hz, 1H); 3.69 (dd, J=12.5 and 4.1 Hz, 1H); 3.15 (dd, J=12.5 and 9.8 Hz, 1H); 1.48 (brs, 2H); 1.41 (brs, 2H); 1.28 (brs, 2H); 1.20 (s, 3H); 1.10 (s, 3H); 0.93 (s, 3H); 0.57 (s, 3H)
$^{13}$C NMR: (CDCl$_3$; 125 MHz): 141.61 (Ar q); 136.68 (Ar q); 129.40 (Ar CH); 128.77 (Ar CH); 127.91 (Ar CH); 127.90 (Ar CH); 127.69 (Ar CH); 125.86 (Ar CH); 85.20 (CH); 59.95 (CH$_2$); 40.43 (CH$_2$); 39.52 (CH$_2$); 20.41 (CH$_3$); 17.18 (CH$_2$)
HRMS (ESI): Calculated for [C$_{23}$H$_{32}$NOS]$^+$ (M$^+$H$^+$): 370.219911; found: 370.220110

1-Phenyl-2-(phenylthio)ethan-1-ol (39)
Isolated as a trace byproduct from reactions between thiophenol and styrene under standard reaction conditions.
**1H NMR:** (CDCl₃; 500 MHz): 7.36-7.15 (m, 10H); 4.65 (ddd, J=9.4, 3.1 and 2.2 Hz, 1H); 3.26 (dd, J=13.8 and 3.5 Hz, 1H); 3.02 (dd, J=13.8 and 9.5 Hz, 1H); 2.79 (d, J=2.2 Hz, 1H)

**13C NMR:** (CDCl₃; 125 MHz): 142.13 (Ar q); 134.84 (Ar q); 130.25 (Ar CH); 129.18 (Ar CH); 128.60 (Ar CH); 128.03 (Ar CH); 126.84 (Ar CH); 125.87 (Ar CH); 71.64 (CH); 44.07 (CH₂)

1-Phenyl-2-(phenylsulfinyl)ethan-1-one (41)

Isolated as a trace byproduct from reactions between thiophenol and styrene under standard reaction conditions.

**1H NMR:** (CDCl₃; 500 MHz): 7.88-7.87 (m, 2H); 7.70-7.68 (m, 2H); 7.59-7.57 (m, 1H); 7.51-7.43 (m, 5H); 4.56 (d, J=14.2 Hz, 1H); 4.29 (d, J=14.2 Hz, 1H)

**13C NMR:** (CDCl₃; 125 MHz): 191.38 (C); 143.33 (Ar q); 136.03 (Ar q); 134.22 (Ar CH); 131.64 (Ar CH); 129.39 (Ar CH); 128.85 (Ar CH); 128.83 (Ar CH); 124.30 (Ar CH); 66.09 (CH₂)

**HRMS (ESI):** Calculated for [C₁₄H₁₂O₂SNa⁺] (M+Na⁺): 267.045022; found: 267.045090

1-Phenyl-2-(phenylsulfinyl)ethan-1-ol (40)

Isolated as a trace byproduct from reactions between thiophenol and styrene under standard reaction conditions.

**1H NMR:** (CDCl₃; 500 MHz, 2 diastereoisomers, dr = 1.1:1): 7.68-7.28 (m, 10H); 5.42 (d, J=10.0 Hz, 1H, minor); 5.25 (d, J=10.3 Hz, 1H, major); 4.22 (d, J=1.5 Hz, 1H, major); 3.99 (d, J=2.7 Hz, 1H, minor); 3.29 (dd, J=13.7 and 10.3 Hz, 1H, major); 3.20 (dd, J=13.2 and 10.0 Hz, 1H, minor); 2.96 (dd, J=13.2 and 2.5 Hz, 1H, minor); 2.84 (dd, J=13.6 and 1.9 Hz, 1H, major)

**13C NMR:** (CDCl₃; 125 MHz, 2 diastereoisomers): 145.31 (Ar q); 144.52 (Ar q); 137.98 (Ar q); 137.15 (Ar q); 131.55 (Ar CH); 131.23 (Ar CH); 129.55 (Ar CH); 129.48 (Ar CH); 128.73 (Ar CH); 128.71 (Ar CH); 128.23 (Ar CH); 128.09 (Ar CH); 125.76 (Ar CH); 125.63 (Ar CH); 124.01 (Ar CH); 123.83 (Ar CH); 76.42 (CH); 69.11 (CH); 64.05 (CH₂); 62.92 (CH₂)

**HRMS (ESI):** Calculated for [C₁₄H₁₄O₂SNa⁺] (M+Na⁺): 269.060672; found: 269.060750
NMR-Spectra
S45
Ph\(\text{SO}_2\)Ph

Bruker VNM-110-01
Zero 21
Time 25.06
Sample 500 MHz
Preparation Depth 150
Channel 1
PPM
Plot 1

Bruker VNM-110-01
Zero 21
Time 25.06
Sample 500 MHz
Preparation Depth 150
Channel 2
PPM
Plot 1

S83
Supplementary References
